

'Patent'

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ENHANCED RECOVERY OF USEFUL
COAL, POTASSIUM CHLORIDE AND BORAX FROM SCREEN BOWL CENTRIFUGE

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FIELD OF THE INVENTION

This invention is in the field of mining and processing of coal, potassium chloride and borax. More particularly this invention concerns the use of polymers to enhance recovery of useful coal, potassium chloride and borax in screen bowl centrifuge separation operations.

BACKGROUND OF THE INVENTION

In processing of coal and potassium chloride and borax it is typical to use a one or more solid-liquid separation stages in order to isolate the desired solids. In all of these mining processing applications, the finest fractions of solid-liquid slurries may be subjected to screen bowl centrifugation for recovery of dewatered solids. The screenbowl centrifuge in a coal or potassium chloride or borax processing plant is used to remove the moisture from the coal or potassium chloride or borax. As part of the moisture removal some of the solids, usually about 40 microns in size, are lost.

The screenbowl centrifuge rotates at a very high rpm. The slurry of coal or potassium chloride or borax enters through the feed pipe and discharges inside the machine. The solids accelerate to the high rpm of the machine and thus encounter high centrifugal forces. This causes the solids to move to the outside of machine and the solids are then moved toward the discharge by an auger. The liquid moves in the opposite direction and discharges as "effluent" at the "bowl drain". The effluent is typically sent to waste and thus the useful coal, potassium chloride or borax in the effluent is lost. That is the waste that mining processing is trying to reduce. A small fraction of the liquid leaves the centrifuge at the screen drain, however, that is not the

fraction of interest in this work because the amount of screen drain liquid is relatively small compared to the effluent and the screen drain liquid typically is recycled back through the process.

The separation inside the machine is made at about 40 microns; greater than about 98% of the +40 micron material reports to the discharge as product along with about 50-70% of the -40 micron material. The remaining about 30-50% of the -40 micron solids report to the effluent and are discarded.

In these separations, it is always a goal to increase the amount of useful coal, potassium chloride and borax that is recovered.

In the past when flocculants were added to the feed prior to entering the machine, the high centrifugal forces inside the machine resulted in the flocculants being sheared, and thus they were not effective in capturing more solids. Therefore, it is widely accepted in the industry that flocculant addition is not effective in reducing the amount of solids being discharged in the effluent.

It would be desirable to identify materials capable of flocculating coal, potassium chloride and borax within the high shear conditions of a centrifuge separation.

SUMMARY OF THE INVENTION

The first aspect of the instant claimed invention is a method of enhancing the recovery of useful coal from screenbowl centrifuge separation operations comprising adding to the screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer, wherein said

cationic terpolymer is prepared by polymerizing from about 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

5 The second aspect of the instant claimed invention is a method of enhancing the recovery of useful potassium chloride from screenbowl centrifuge separation operations comprising adding to the screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer to the screenbowl centrifuge, wherein said cationic terpolymer is prepared by polymerizing from about
10 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

 The third aspect of the instant claimed invention is a method of enhancing the recovery of useful borax from screenbowl centrifuge separation operations comprising adding to the
15 screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer, wherein said cationic terpolymer is prepared by polymerizing from about 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic
20 monomers.

DETAILED DESCRIPTION OF THE INVENTION

Throughout this patent application, the following terms have the indicated meanings.

5 “AM” means acrylamide.

 "Alkyl" means a monovalent group derived from a straight or branched chain saturated hydrocarbon by the removal of a single hydrogen atom. Representative alkyl groups include methyl, ethyl, *n*- and *iso*-propyl, and the like.

 “Alkylene” means a divalent group derived from a straight or branched chain saturated
10 hydrocarbon by the removal of two hydrogen atoms. Representative alkylene groups include methylene, ethylene, propylene, and the like.

 “Based on polymer active” and “based on monomer” mean the amount of a reagent added based on the level of vinylic monomer in the formula, or the level of polymer formed after polymerization, assuming 100% conversion.

15 “Based on formula” means the amount of reagent added based on the total formula weight.

 “borax” is a natural hydrated sodium borate, (either 5 or 10 H₂O) that is found in salt lakes and alkali soils. It is also the commercial name for sodium borate.

 “Cationic Monomer” means a monomer, as defined herein, which possesses a net positive
20 charge. Representative cationic monomers include dialkylaminoalkyl acrylates and methacrylates and their quaternary or acid salts, including, but not limited to, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate

sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts such as acrylamidopropyltrimethylammonium chloride, dimethylaminopropylacrylamide methyl sulfate quaternary salt, dimethylaminopropylacrylamide sulfuric acid salt, dimethylaminopropylacrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropylmethacrylamide methyl sulfate quaternary salt, dimethylaminopropylmethacrylamide sulfuric acid salt, dimethylaminopropylmethacrylamide hydrochloric acid salt, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, diallyldiethylammonium chloride and diallyldimethyl ammonium chloride. Alkyl groups are generally C₁₋₄ alkyl.

“Chain Transfer Agent” means any molecule, used in free-radical polymerization, which will react with a polymer radical forming a dead polymer and a new radical. Representative Chain Transfer Agents are listed by K. C. Berger and G. Brandrup, “*Transfer Constants to Monomer, Polymer, Catalyst, Solvent, and Additive in Free Radical Polymerization*,” Section II, pp. 81-151, in “*Polymer Handbook*,” edited by J. Brandrup and E. H. Immergut, 3d edition, 1989, John Wiley & Sons, New York. Preferred chain transfer agents include sodium formate, 2-mercaptoethanol and isopropanol. Sodium formate is more preferred.

“Coal” means a natural, solid, combustible material formed from prehistoric plant life which occurs in layers or veins in sedimentary rocks. Chemically, coal is a macromolecular

network composed of groups of polynuclear aromatic rings, to which are attached subordinate rings connected to oxygen, sulfur and aliphatic bridges.

“Dispersion polymer” means a dispersion of fine particles of polymer in an aqueous salt solution which is prepared by polymerizing monomers with stirring in an aqueous salt solution in which the resulting polymer is insoluble. *See* U.S. Pat. nos. 5,708,071; 4,929,655; 5,006,590; 5,597,859; 5,597,858 and European Patent nos. 657,478 and 630,909.

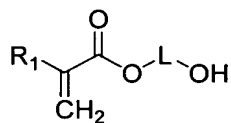
In a typical procedure for preparing a dispersion polymer, an aqueous solution containing one or more inorganic or hydrophobic salts, one or more water-soluble monomers, any polymerization additives such as processing aids, chelants, pH buffers and a water-soluble stabilizer polymer is charged to a reactor equipped with a mixer, a thermocouple, a nitrogen purging tube, and a water condenser. The monomer solution is mixed vigorously, heated to the desired temperature, and then a water-soluble initiator is added. The solution is purged with nitrogen while maintaining temperature and mixing for several hours. After this time, the mixture is cooled to room temperature, and any post-polymerization additives are charged to the reactor. Water continuous dispersions of water-soluble polymers are free flowing liquids with product viscosities generally 100-10,000 cP, measured at low shear.

“Gel polymer” means a polymer made by gel polymerization. In a typical procedure for preparing gel polymers, an aqueous solution containing one or more water-soluble monomers and any additional polymerization additives such as chelants, pH buffers, and the like, is prepared. This mixture is charged to a reactor equipped with a mixer, a thermocouple, a nitrogen purging tube and a water condenser. The solution is mixed vigorously, heated to the desired temperature, and then one or more water-soluble free radical polymerization initiators are added. The solution is purged with nitrogen while maintaining temperature and mixing for several hours. Typically,

the viscosity of the solution increases during this period. After the polymerization is complete, the reactor contents are cooled to room temperature and then transferred to storage. Gel polymer viscosities vary widely, and are dependent upon the concentration and molecular weight of the active polymer component. Gel polymers may be dried to yield dry polymers.

5 “DMAEA*MCQ” means dimethylaminoethyl acrylate methyl chloride quaternary salt. This may also be abbreviated “DMAEA.MCQ”.

 “Hydroxyalkyl (meth)acrylate” means a compound of formula



where R₁ is H or CH₃ and L is C₁-C₈, preferably C₁-C₄ alkylene. Representative hydroxyalkyl
10 (meth)acrylates include hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, 6-hydroxyhexyl methacrylate, and the like.

 “Latex polymer” means a water-in-oil polymer emulsion comprising a cationic terpolymer according to this invention in the aqueous phase, a hydrocarbon oil for the oil phase
15 and one or more water-in-oil emulsifying agents. Latex polymers are hydrocarbon continuous with the water-soluble polymers dispersed within the hydrocarbon matrix. The latex polymer is “inverted” or activated for use by releasing the polymer from the particles using shear, dilution, and, generally, another surfactant. See U.S. Pat. No. 3,734,873, incorporated herein by reference. Representative preparations of high molecular weight inverse emulsion polymers are described in
20 U. S. Patent No.’s 2,982,749; 3,284,393; and 3,734,873. See also, “Mechanism, Kinetics and Modeling of the Inverse-Microsuspension Homopolymerization of Acrylamide,” Hunkeler, et al., Polymer (1989), 30(1), 127-42; and “Mechanism, Kinetics and Modeling of Inverse-

Microsuspension Polymerization: 2. Copolymerization of Acrylamide with Quaternary Ammonium Cationic Monomers,” Hunkeler et al., Polymer (1991), 32(14), 2626-40.

Inverse emulsion polymers are prepared by dissolving the desired monomers and any polymerization additives such as inorganic salts, chelants, pH buffers, and the like in the aqueous phase, dissolving the emulsifying agent(s) in the oil phase, emulsifying the water phase in the oil phase to prepare a water-in-oil emulsion, in some cases, homogenizing the water-in-oil emulsion, polymerizing the monomers dissolved in the water phase of the water-in-oil emulsion to obtain the polymer as a water-in-oil emulsion. If so desired, a self-inverting surfactant can be added after the polymerization is complete in order to obtain the water-in-oil self-inverting emulsion.

The oil phase comprises any inert hydrophobic liquid. Preferred hydrophobic liquids include aliphatic and aromatic hydrocarbon liquids including benzene, xylene, toluene, paraffin oil, coal, potassium chloride or borax spirits, kerosene, naphtha, and the like. A paraffinic oil is preferred.

Free radical yielding initiators such as benzoyl peroxide, lauroyl peroxide, 2,2'-azobis (isobutyronitrile) (AIBN), 2,2'-azobis(2,4-dimethylvaleronitrile) (AIVN), potassium persulfate and the like are useful in polymerizing vinyl and acrylic monomers. 2,2'-azobis(isobutyronitrile) (AIBN) and 2,2'-azobis(2,4-dimethylvaleronitrile) (AIVN) are preferred. The initiator is utilized in amounts ranging between about 0.002 and about 0.2 percent by weight of the monomers, depending upon the solubility of the initiator.

Water-in-oil emulsifying agents useful for preparing latex polymers include sorbitan esters of fatty acids, ethoxylated sorbitan esters of fatty acids, and the like or mixtures thereof. Preferred emulsifying agents include sorbitan monooleate, polyoxyethylene sorbitan monostearate, and the like. Additional details on these agents may be found in McCutcheon's

Detergents and Emulsifiers, North American Edition, 1980. Any inverting surfactant or inverting surfactant mixture described in the prior art may be used. Representative inverting surfactants include ethoxylated nonylphenol, ethoxylated linear alcohols, and the like. Preferred inverting surfactants are ethoxylated linear alcohols.

5 The polymer is prepared by polymerizing the appropriate monomers at a temperature of from about 30°C to about 85°C over about 1 to about 24 hours, preferably at a temperature of from about 40°C to about 70°C over about 3 to about 6 hours. Upon completion of the reaction, the water-in-oil emulsion polymer is cooled to room temperature, where any desired post-polymerization additives, such as antioxidants, or a high HLB surfactant (as described in U.S.
10 Patent 3,734,873) may be added.

 The resulting emulsion polymer is a free-flowing liquid. An aqueous solution of the water-in-oil emulsion polymer can be generated by adding a desired amount of the emulsion polymer to water with vigorous mixing in the presence of a high-HLB surfactant (as described in U.S. Patent 3,734,873).

15 “lbs” means pounds. One pound is equal to 454 grams is equal 0.454 kilograms.

 “Monomer” means a polymerizable allylic, vinylic or acrylic compound. The monomer may be cationic or nonionic. Vinyl monomers are preferred, acrylic monomers are more preferred.

 “Nalco” means Nalco Company, 1601 W. Diehl Road, Naperville, IL 60563. (630) 305-
20 1000.

 “Nonionic monomer” means a monomer as defined herein which is electrically neutral. Representative non-ionic, water-soluble monomers include acrylamide, methacrylamide, *N,N*-dimethylacrylamide, *N,N*-diethylacrylamide, *N*-isopropylacrylamide, *N*-vinylformamide,

N-vinylmethacetamide, *N*-vinyl pyrrolidone, *N*-*t*-butylacrylamide, *N*-methylolacrylamide, and the like. Preferred nonionic monomers are acrylamide and methacrylamide. Acrylamide is more preferred.

“potassium chloride” is KCl, Chemical Abstract Services Registry No. 7447-40-7. For purposes of this patent application the word “Potash” is understood to be a source of potassium chloride. Potash is currently being mined in New Mexico, U.S.A. and in Saskatchewan, Canada.

“RSV” stands for Reduced Specific Viscosity. The RSV of a polymer solution is a measure of the capacity of polymer molecules to enhance the viscosity of the solution at a given concentration, which depends on the structure of the polymer molecules (including size and shape), and interaction between polymer molecules. Within a series of polymer homologs which are substantially linear and well solvated, “reduced specific viscosity (RSV)” measurements for dilute polymer solutions are an indication of polymer chain length and average molecular weight according to Paul J. Flory, in “*Principles of Polymer Chemistry*”, Cornell University Press, Ithaca, NY., 1953, Chapter VII, “*Determination of Molecular Weights*”, pp. 266-316. The RSV is measured at a given polymer concentration and temperature and calculated as follows:

$$RSV = \frac{\left[\left(\frac{\eta}{\eta_o}\right) - 1\right]}{c}$$

wherein η = viscosity of polymer solution;

η_o = viscosity of solvent at the same temperature; and

c = concentration of polymer in solution.

The units of concentration “ c ” are (grams/100 ml or g/deciliter). Therefore, the units of RSV are dL/g. In this patent application, for measuring RSV, the solvent used is 1.0 molar sodium nitrate solution. The polymer concentration in this solvent is 0.045 g/dL. The RSV is measured at 30

°C. The viscosities η and η_0 are measured using a Cannon Ubbelohde semimicro dilution viscometer, size 75. The viscometer is mounted in a perfectly vertical position in a constant temperature bath adjusted to 30 ± 0.02 °C. The error inherent in the calculation of RSV is about 2 dl/grams. When two polymer homologs within a series have similar RSV's that is an indication that they have similar molecular weights.

"ton" means 2000 pounds.

The instant claimed invention is a method of enhancing the recovery of useful mined materials from screenbowl centrifuge separation operations comprising adding to the screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer, wherein said cationic terpolymer is prepared by polymerizing from about 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

The useful mined materials are selected from the group consisting of coal, potassium chloride and borax.

The screenbowl centrifuge separation operations can be any part of the coal, potassium chloride or borax process where a screenbowl centrifuge is used in the separation. For instance, in coal processing, typically the screenbowl centrifuge in a coal processing plant is used to remove the moisture from the coal, prior to the finished coal leaving the coal processing plant.

The streams associated with a screenbowl include the feed, the effluent, the screen drain and the product.

"Feed" is the minus 1 mm material at 25-35% solids that enters the screenbowl. The flow varies from about 350 to about 800 gallons per minute depending on the size of the

machine. The percent solids can vary from about 20% to about 40% and the tons per hour of solids can be from about 20 to about 80.

“Effluent” is the water and fine solids that are removed from the coal. The solids in the effluent are usually 96-98% minus 40 microns. The flow can be 250-500 gpm and the tons/hr of solids depends upon the % solids. This material normally reports to the refuse thickener for disposal. This is the material that the instant claimed invention is directed to as the instant claimed invention will permit more useful coal or potassium chloride or borax to leave the screen bowl centrifuge with the product instead of leaving the screen bowl centrifuge with the effluent.

“Screen Drain” is entrained water and fine solids that are removed just prior to the coal discharging the machine. The flow is usually small, about 5% of the feed flow, and this material is recycled back into the plant.

“Product” is the dried coal or the dried potassium chloride or the dried borax to be sold.

The screenbowl rotates at a very high rpm. The coal slurry enters through the feed pipe and discharges inside the machine. The solids accelerate to the high rpm of the machine and thus encounter high centrifugal forces. This causes the solids to move to the outside of machine and the solids are then moved toward the discharge by an auger. The liquid moves in the opposite direction and discharges at the feed end. The separation inside the machine is made at about 40 microns; greater than 98% of the +40 micron material reports to the discharge as product along with about 50-60% of the -40 micron material. The remaining 40-50% of the -40 micron solids report to the effluent and are discarded.

The cationic terpolymers are added to the screenbowl for the purpose of capturing more of the solids from the effluent and thus having it report with the Product. In the past when

flocculants were added to the feed prior to entering the machine, the high forces inside the machine resulted in the flocculants being sheared, and thus they were not effective in capturing more solids. Therefore, it was widely accepted in the industry that any type of flocculant addition was not effective in reducing the amount of solids being discharged in the effluent. In contrast to what was believed to be true, with use of the cationic terpolymers described herein, it has been found possible to enhance the recovery of desired coal, potassium chloride or borax by using the cationic terpolymers in centrifuge separation operations.

The cationic terpolymers can be made by latex polymerization, gel polymerization and dispersion polymerization techniques. It is preferred that they be made by latex polymerization, for convenience of application, and thus latex polymers are preferred for use in the instant claimed invention.

Regarding the polymers, the cationic polymers useful in the instant claimed invention are prepared by polymerizing from about 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

In one preferred aspect, the cationic polymer is prepared by polymerizing from about 20 to about 80 mole percent of one or more cationic monomers, from about 1 to about 2.5 mole percent of one or more hydroxyalkyl (meth)acrylates and from 17.5 to about 79 mole percent of one or more nonionic monomers.

In another preferred aspect the cationic monomer is selected from the group comprising dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, acrylamidopropyltrimethylammonium chloride and

methacrylamidopropyltrimethylammonium chloride. Dimethylaminoethyl acrylate methyl chloride quaternary salt is the most preferred cationic monomer.

In another preferred aspect, the hydroxyalkyl (meth)acrylate is selected from hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and 6-hydroxyhexyl methacrylate. 2-Hydroxyethyl methacrylate (hereinafter "HEMA") and 2-hydroxypropyl methacrylate are more preferred. HEMA is the most preferred hydroxyalkyl(meth)acrylate.

In another preferred aspect of this invention, the nonionic monomers are selected from acrylamide and methacrylamide and the cationic monomers are selected from dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, acrylamidopropyltrimethylammonium chloride and methacrylamidopropyltrimethylammonium chloride.

In another preferred aspect, the nonionic monomer is acrylamide and the cationic monomer is dimethylaminoethyl acrylate methyl chloride quaternary salt and the hydroxyalkyl (meth)acrylate is hydroxyethyl methacrylate.

The cationic terpolymers useful in the instant claimed invention are either available commercially or may be synthesized using techniques known to people of ordinary skill in the art. See U.S. Patent No. 6,627,719 B2, entitled CATIONIC LATEX TERPOLYMERS FOR SLUDGE DEWATERING, which issued on September 30, 2003. U.S. Patent No. 6,627,719 B2 is incorporated by reference in its entirety.

Cationic terpolymers of the following formulas are available from Nalco.

Polymer	A	B	C	D	E
Mole % AM	70	49	34	20	50
Mole % DMAEA*MCQ	29	49	64	78	49
Mole % HEMA	1	2	2	2	1
Total Mole %	100	100	100	100	100

The total amount of polymer required to effectively enhance the recovery of useful coal, potassium chloride or borax from centrifuge separation may vary considerably according to the characteristics of the material being fed into the screenbowl centrifuge and the degree of processing in the centrifuge required.

Typically, the polymer is added in an amount of from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, preferably from about 0.04 lbs active polymer/ton dry solids into centrifuge to about 0.68 lbs active polymer/ton dry solids in centrifuge, and more preferably from about 0.1 lbs active polymer/ton dry solids in centrifuge to about 0.3 lbs active polymer/ton dry solids into centrifuge based on polymer actives.

The dose of polymer based on lbs active polymer/lbs slurry in centrifuge, expressed in ppm, is as follows: the polymer is added in an amount of from about 5 ppm to about 125 ppm, preferably from about 10 ppm to about 100 ppm and more preferably from about 20 ppm to about 80 ppm based on polymer actives.

To enhance the efficacy of the cationic terpolymers of the instant claimed invention it is recommended to add the polymers inside the centrifuge in a low-shear zone to allow the solids to be flocculated without being torn apart by the shear forces. Preferably, the polymers are added

after water and fine sized solids were separated from the larger coal particle. It is not recommended to add the polymers with the feed into the screenbowl centrifuge because if this is done, then any positive effect the polymers have upon the feed in terms of flocculation will be negated when the newly formed flocs encounter the severe shear in the centrifuge.

5 Addition of polymer to centrifuge may be through pipes or drop chutes or any other technique known in the art.

In addition to enhancing the recovery of coal, use of the cationic terpolymers of this invention has also been found possible to enhance the recovery of potassium chloride and borax.

10 The second aspect of the instant claimed invention is a method of enhancing the recovery of useful potassium chloride from screenbowl centrifuge separation operations comprising adding to the screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer, wherein said cationic terpolymer is prepared by polymerizing from about 1 to about 99.1 mole percent of one or more cationic monomers, from about 0.1 to about 10 mole percent of one or more
15 hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

Potassium chloride is mined from sylvite deposits, known as Potash, in New Mexico and Saskatchewan and purified by fractional crystallization or flotation. It can also be crystallized from salt lake brine and purified by recrystallization. A thorough review article of processing of
20 potash in the mines of Saskatchewan can be found in CIM Bulletin, Vol. 96, No. 1070, pgs. 61-65, "Potash Processing in Saskatchewan--A review of process technologies" by C. F. Perucca, April 2003.

When potash is being processed to yield potassium chloride, screen-bowl centrifuges are used to de-brine the concentrates from flotation bearing the valuable coal, potassium chloride or borax. The concentrate is then dried and compacted to afford granular product for fertilizer applications or is redissolved and crystallized to afford industrial grade potassium chloride.

5 The third aspect of the instant claimed invention is a method of enhancing the recovery of useful borax from screenbowl centrifuge separation operations comprising adding to the screenbowl centrifuge, from about 0.03 lbs active polymer/ton dry solids in centrifuge to about 0.70 lbs active polymer/ton dry solids in centrifuge, of a cationic terpolymer, wherein said cationic terpolymer is prepared by polymerizing from about 1 to about 99.1 mole percent of one
10 or more cationic monomers, from about 0.1 to about 10 mole percent of one or more hydroxyalkyl (meth)acrylates and from one to about 98.1 mole percent of one or more nonionic monomers.

Borax is a naturally hydrated sodium borate found in salt lakes and alkali soils. When borax is being processed, mud tailings are concentrated in screen bowl centrifuges for
15 impoundment.

The performance of the cationic terpolymers of this invention may be monitored by means of an inert fluorescent tracer as described in U.S. Patent. No. 4,783,314, incorporated herein by reference. In particular, a composition comprising a cationic terpolymer according to this invention and an inert fluorescent tracer compound in a known ratio is added to the
20 screenbowl centrifuge containing the coal, potassium chloride or borax slurry as described above. The fluorescent signal of the coal, potassium chloride or borax slurry is detected and measured using one or more fluorometers and used to quantify and control the amount and feed rate of the

polymer to achieve the desired amount of cationic terpolymer in the coal, potassium chloride or borax slurry.

“Inert fluorescent tracer compound” means a material which is capable of fluorescing while present in the sludge being treated. The inert fluorescent tracer compound should not be appreciably affected by any other material present in the coal, potassium chloride or borax slurry, or by the temperature or temperature changes encountered during the dewatering process. Inert fluorescent tracers suitable for use with the cationic terpolymers of the instant claimed invention are selected from the group comprising:

1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl)-D- ribitol, also known as Riboflavin or Vitamin B2 (CAS Registry No. 83-88-5),

fluorescein (CAS Registry No. 2321-07-5),

fluorescein, sodium salt (CAS Registry No. 518-47-8, aka Acid Yellow 73, Uranine),

2-anthracenesulfonic acid sodium salt (CAS Registry No. 16106-40-4),

1,5-anthracenedisulfonic acid (CAS Registry No. 61736-91-2) and salts thereof,

2,6-anthracenedisulfonic acid (CAS Registry No. 61736-95-6) and salts thereof,

1,8-anthracenedisulfonic acid (CAS Registry No. 61736-92-3) and salts thereof,

mono-, di-, or tri-sulfonated naphthalenes, including but not limited to

1,5-naphthalenedisulfonic acid, disodium salt (hydrate) (CAS Registry No. 1655-29-4, aka 1,5-NDSA hydrate),

2-amino-1-naphthalenesulfonic acid (CAS Registry No. 81-16-3),

5-amino-2-naphthalenesulfonic acid (CAS Registry No. 119-79-9),

4-amino-3-hydroxy-1-naphthalenesulfonic acid (CAS Registry No. 90-51-7),

6-amino-4-hydroxy-2-naphthalenesulfonic acid (CAS Registry No. 116-63-2),

7-amino-1,3-naphthalenesulfonic acid, potassium salt (CAS Registry No. 79873-35-1),

- 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid (CAS Registry No. 90-20-0),
 5-dimethylamino-1-naphthalenesulfonic acid (CAS Registry No. 4272-77-9),
 1-amino-4-naphthalene sulfonic acid (CAS Registry No. 84-86-6),
 1-amino-7-naphthalene sulfonic acid (CAS Registry No. 119-28-8), and
 5 2,6-naphthalenedicarboxylic acid, dipotassium salt (CAS Registry No. 2666-06-0),
 3,4,9,10-perylenetetracarboxylic acid (CAS Registry No. 81-32-3),
 C.I. Fluorescent Brightener 191, also known as, Phorwite CL (CAS Registry No. 12270-53-0),
 10 C.I. Fluorescent Brightener 200, also known as Phorwite BKL (CAS Registry No. 61968-72-7),
 benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-(4-phenyl-2H-1,2,3-triazol-2-yl)-, dipotassium salt, also known as Phorwite BHC 766 (CAS Registry No. 52237-03-3),
 benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt, also
 15 known as Pylaklor White S-15A (CAS Registry No. 6416-68-8),
 1,3,6,8-pyrenetetrasulfonic acid, tetrasodium salt (CAS Registry No. 59572-10-0),
 pyranine, (CAS Registry No. 6358-69-6, aka 8-hydroxy-1, 3, 6-pyrenetrisulfonic acid, trisodium salt),
 quinoline (CAS Registry No. 91-22-5),
 20 3H-phenoxazin-3-one, 7-hydroxy-, 10-oxide, also known as Rhodalux (CAS Registry No. 550-82-3),
 xanthylum, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium salt, also known as Rhodamine WT (CAS Registry No. 37299-86-8),
 phenazinium, 3,7-diamino-2,8-dimethyl-5-phenyl-, chloride, also known as Safranin O (CAS
 25 Registry No. 477-73-6),
 C.I. Fluorescent Brightener 235, also known as Sandoz CW (CAS Registry No. 56509-06-9),

benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt, also known as Sandoz CD (CAS Registry No. 16470-24-9, aka Flu. Bright. 220),

5 benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(2-hydroxypropyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt, also known as Sandoz TH-40 (CAS Registry No. 32694-95-4),

xanthylum, 3,6-bis(diethylamino)-9-(2,4-disulfophenyl)-, inner salt, sodium salt, also known as Sulforhodamine B (CAS Registry No. 3520-42-1, aka Acid Red 52),

10 benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(aminomethyl)(2-hydroxyethyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt, also known as Tinopal 5BM-GX (CAS Registry No. 169762-28-1),

Tinopol DCS (CAS Registry No. 205265-33-4),

benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyl)-2,1-ethenediyl)bis-, disodium salt, also known as Tinopal CBS-X (CAS Registry No. 27344-41-8),

15 benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt, also known as Tinopal RBS 200, (CAS Registry No. 6416-68-8),

7-benzothiazolesulfonic acid, 2,2'-(1-triazene-1,3-diyl)-4,1-phenylene)bis[6-methyl-, disodium salt, also known as Titan Yellow (CAS Registry No. 1829-00-1, aka Thiazole Yellow G), and

20 all ammonium, potassium and sodium salts thereof, and all like agents and suitable mixtures thereof.

The more preferred fluorescent inert tracers of the present invention include 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (CAS Registry No. 59572-10-0); 1,5-naphthalenedisulfonic acid disodium salt (hydrate) (CAS Registry No. 1655-29-4, aka 1,5 – NDSA hydrate); xanthylum, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium

salt, also known as Rhodamine WT (CAS Registry No. 37299-86-8); 1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl)-D- ribitol, also known as Riboflavin or Vitamin B2 (CAS Registry No. 83-88-5); fluorescein (CAS Registry No. 2321-07-5); fluorescein, sodium salt (CAS Registry No. 518-47-8, aka Acid Yellow 73, Uranine); 2-anthracenesulfonic acid sodium salt (CAS Registry No. 16106-40-4); 1,5-anthracenedisulfonic acid (CAS Registry No. 61736-91-2) and salts thereof; 2,6-anthracenedisulfonic acid (CAS Registry No. 61736-95-6) and salts thereof; 1,8-anthracenedisulfonic acid (CAS Registry No. 61736-92-3) and salts thereof; and mixtures thereof. The fluorescent tracers listed above are commercially available from a variety of different chemical supply companies.

The most preferred inert fluorescent tracer compound is 1,3,6,8-pyrenetetrasulfonic acid, sodium salt.

The cationic terpolymer/inert fluorescent tracer compound composition is prepared by adding the inert fluorescent tracer compound with stirring to the cationic terpolymer of this invention. An inverting surfactant as described herein may be added along with the inert fluorescent tracer compound. The amount of inert fluorescent tracer compound added may be readily determined by one of ordinary skill in the art, taking into consideration the polymer composition and the characteristics of the sludge being treated.

One or more fluorometers are used to detect the fluorescent signal of the inert fluorescent tracers. Suitable fluorometers are selected from the group comprising Examples of fluorometers that may be used in the practice of this invention include the TRASAR® 3000 fluorometer, the TRASAR® 8000 fluorometer and the TRASAR® XE-2 Controller, which includes a fluorometer with integrated controller, all available from Nalco; the Hitachi F-4500 fluorometer (available from Hitachi through Hitachi Instruments Inc. of San Jose, CA); the JOBIN YVON FluoroMax-3

“SPEX” fluorometer (available from JOBIN YVON Inc. of Edison, NJ); and the Gilford Fluoro-IV spectrophotometer or the SFM 25 (available from Bio-tech Kontron through Research Instruments International of San Diego, CA). It should be appreciated that the fluorometer list is not comprehensive and is intended only to show examples of fluorometers. Other commercially
5 available fluorometers and modifications thereof can also be used in this invention.

After the fluorometer has been used to detect the fluorescent signal of the inert fluorescent tracer then the detected fluorescent signal can be converted into the actual concentration of inert fluorescent tracer using graphs that show what the detected fluorescent signal is for a specific amount of a specific inert fluorescent tracer. These graphs are known to people of ordinary skill
10 in the art of fluorometry.

Because the inert fluorescent tracer is added to the screen bowl centrifuge in a known proportion to the cationic terpolymer, by detecting the fluorescent signal of the inert fluorescent tracer it is possible to calculate the amount of cationic terpolymer present either in the screen bowl centrifuge or in the effluent or even in the screen drain. This enables the operator to
15 determine whether the correct amount of cationic terpolymer is present and even to determine where it is present. If desired, adjustments to the operating conditions of the screenbowl centrifuge can be made to ensure the amount of cationic terpolymer present is what is supposed to be present.

The third aspect of the instant claimed invention is the method of the first aspect of the
20 instant claimed invention wherein an inert fluorescent tracer is added to the cationic terpolymer and one or more fluorometers are used to detect the fluorescent signal of the inert fluorescent tracer, which fluorescent signal is used to determine how much inert fluorescent tracer is present and that information is used to determine how much cationic terpolymer is present and by

knowing how much cationic terpolymer is present then if desired, adjustments to the operating conditions of the screenbowl centrifuge can be made to ensure the desired amount of cationic terpolymer is present.

5 The fourth aspect of the instant claimed invention is the method of the second aspect of the instant claimed invention wherein an inert fluorescent tracer is added to the cationic terpolymer and one or more fluorometers are used to detect the fluorescent signal of the inert fluorescent tracer, which fluorescent signal is used to determine how much inert fluorescent tracer is present and that information is used to determine how much cationic terpolymer is present and by knowing how much cationic terpolymer is present, then if desired, adjustments to
10 the operating conditions of the screenbowl centrifuge can be made to ensure the desired amount of cationic terpolymer is present.

The fifth aspect of the instant claimed invention is the method of the third aspect wherein an inert fluorescent tracer is added to the cationic terpolymer and one or more fluorometers are used to detect the fluorescent signal of the inert fluorescent tracer, which fluorescent signal is
15 used to determine how much inert fluorescent tracer is present and that information is used to determine how much cationic terpolymer is present and by knowing how much cationic terpolymer is present, then if desired, adjustments to the operating conditions of the screenbowl centrifuge can be made to ensure the desired amount of cationic terpolymer is present.

The following examples are intended to be illustrative of the present invention and to
20 teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

Example 1

The screening test for the cationic terpolymers in the method of the instant claimed invention is as follows:

A mixture of 40 cc of slurry and cationic terpolymer, at the desired dose, is charged into a
5 50 mL centrifuge tube. The contents of the tube are mixed on a Fisher Vortex Genie 2™ from
Fisher Scientific, dialed to 6.5 of 8 for 10 seconds. This vortex mixing is followed by
centrifugation, using a Model HN-S centrifuge from International Equipment Company,
Needham Heights, Massachusetts, set at Full, which reads as 2700 revolutions per minute on the
tach dial for 1 min. After one minute the centrifuge is 'dialed off' and the break is applied.
10 Following centrifugation, the contents of the tube are mixed again for 10 seconds with the same
vortex mixer used previously at the same settings, at which time the nature of the floc formed is
observed.

In this screening study a coal slurry is used. The cationic polymers are as follows:
Polymer A is 70 mol percent AM/29 mol percent DMAEA.MCQ/1 mol percent HEMA,
15 Polymer B is 49 mol percent AM/49 mol percent DMAEA.MCQ/2 mol percent HEMA,
Polymer C is 34 mol percent AM/64 mol percent DMAEA.MCQ/2 mol percent HEMA.

Example	Polymer	Mole % Charge	lbs active product per dry ton of coal	Observations @10 seconds	Additional Observations
1	A	30	0.4	Clear supernatant, Completely "flocked". Compacted flock held together	
2	A	30	0.4	Compaction broke up after 10 seconds. Very fine flocks	
3	C	65	0.4	Clear supernatant, Completely "flocked". Compacted flock held together	
4	C	65	0.4	Clear supernatant, Completely "flocked". Compacted flock held together	Held together until after an additional 35 seconds, dislodged large flocks. Left half the "cake"
5	C	65	0.4	Very small amount of medium sized after 9 seconds, most of flocked coal remained compacted	Held together until after an additional 21 seconds, then broke and blackened water. Left third of "cake"
6	C	65	0.4	Clear supernatant, Completely "flocked". Compacted flock held together	Very small amount of medium sized after 11 seconds. Held together until after an additional 31 seconds, then broke and blackened water. Left third of "cake"
7	C	65	0.4	Very small amount of medium sized after 8 seconds, most of flocked coal remained compacted	Held together until after an additional 18 seconds, then broke. Left two thirds of "cake"
8	B	50	0.4	In two runs, Compaction broke up after 5-7 seconds.	

The observations recorded in this table show that the indicated cationic terpolymers are effective in flocculating the coal in the slurry under the harsh vibration-centrifugation-vibration conditions of the test.

5 By using this screening test, it is found that polymers that perform well in high-shear field applications are those that have the ability to form a large floc when mixed on the vortex mixer prior to and following centrifugation.

In a large scale coal processing plant for example, the recovered fine coal is saleable and would afford an additional source of revenue. As an example, a typical coal production plant site can process about 6,000 tons/day through the screen bowl centrifuges. The improvement in
10 effluent solids described here would afford about 150 tons/day, currently saleable at about \$15-\$30/ton.

Various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its
15 attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.